

COATINGS

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THE PROPERTIES OF GLASS COMPOSITES WITH NANOCOATINGS: DEPENDENCE ON THE PRODUCTION TECHNOLOGY PARAMETERS

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The changes in the thickness and index of refraction of one-component coatings comprised of SiO₂ and TiO₂ deposited from solutions onto a sheet float-glass substrate and the light transmittance of the composites as a function of the film-deposition conditions are studied. The effects of the oxide content in solution and the deposition rate and maturation time of the solutions are determined quantitatively on the basis of the properties of the films and composites.

Key words: oxide nanocoating, film-forming solution, composite, consisting of sheet glass with a nanocoating on the surface, light transmittance, light losses, film thickness, index of refraction.

Composites consisting of a substrate comprised of optical or technical glass with a 50 to 500 nm or more thick nanocoating are successfully used to change different properties of glass (optical, mechanical, physical-chemical and others) and thereby extend the range of application of the material [1 – 4].

Of the known methods of producing such composites the deposition of a coating comprised of solutions of hydrolyzing compounds (sols) on a substrate merits special consideration. The generally accepted name for this method is sol-gel technology.

Several basic parameters can be singled out in the sol-gel technology – the form of the initial materials used to make sols, their content (by weight) of film-forming oxides and the maturation time and deposition rate of the solution, by changing which the performance of the composites can be controlled [5 – 7].

Single-component coatings consisting of low- or high-index oxides SiO₂ and TiO₂ are used quite often to modify a glass surface, specifically, adjust its optical properties. Previous studies have shown that the properties of composites

with coatings from two- or three-component oxide systems [8, 9] are very sensitive to the conditions of preparation, maturation and deposition of film-forming solutions (FFS). The aim of the present work is to make qualitative and quantitative assessments of the effect of film-forming oxides in solution and the maturation time of FFS on the thickness and refractive index of the coatings and the light-transmittance of the composites sheet glass — SiO₂ or TiO₂ film.

Solution Preparation and Control. The starting materials (Table 1) were hydrolyzing compounds — silicon and titanium tetroxides. The solvents were alcohols, hydrolysis was acidic and the catalyst of hydrolysis was analytical grade hydrochloric acid (GOST 3118–77).

The oxide content (by weight) in the solutions (sols) was as follows: SiO₂, increasing from 2.5 to 7.5%⁴ and TiO₂ from 2.5 to 5%. The maturation times of the sols were 2 and 47 days for SiO₂ and 2 and 14 days for TiO₂. The solutions were kept at room temperature. The kinematic viscosity of the sols was monitored with a VPZh-1 viscometer and the light transmittance in the 20 mm thick layer was monitored at the wavelengths 315, 364, 400, 440 and 540 nm (KFK-3 photometer).

Fabrication and Control of Composites. Bilateral coatings were deposited by immersing in the film-forming solu-

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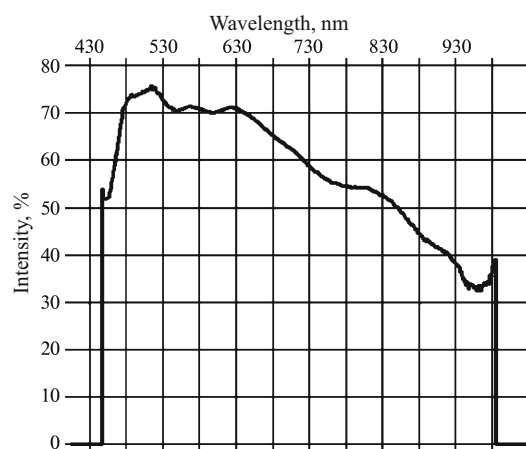
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⁴ Here and below, the content by weight, unless stipulated otherwise.

TABLE 1. Materials for the Film-Forming Solutions (FFS)

Coating	Hydrolyzing compound	Solvent
SiO ₂	Tetraethoxysilane (TEOS), Si(OC ₂ H ₅) ₄ , analytical grade according to TU 6-09-11-2153-94, vers. 1, 2	Ethanol C ₂ H ₅ OH. Drinkable ethyl alcohol 95%, GOST R 51723-2001
TiO ₂	Tetraethoxytitanium (TET), Ti(OC ₂ H ₅) ₄ , analytical grade according to TU 2423-023-5028-4764-2006	Isopropanol (CH ₃) ₂ CHOH, chemically pure grade, TU 2632-015-11291058-95

**Fig. 1.** Spectral curve of the light transmittance of a TiO₂-coated glass composite.

tions 50 × 50 mm, 4 mm thick samples of float-glass (M1 grade according to GOST 101-90) cut from the same 3 × 6 m sheet.

The rate of extraction of the substrates from the solutions was maintained strictly constant in definite cycles and was varied from 3.8 to 17.3 mm/sec for different samples. The immersed samples were allowed to stand in air for 1 – 1.5 h in order to complete hydrolysis, polycondensation, evaporation of the solvent and drying of the coating, after which the samples were placed for 20 min into a microwave furnace to fix the film.

After the samples cooled down the light transmittance T of the composite was measured with a FSD-8 spectrophotometer (developed and built at the Institute of General Physics of the Russian Academy of Sciences) and the average value T_{av} in the visible region of the spectrum in the wavelength range 450 – 720 nm was calculated. As an example a plot of the spectral dependence of the light transmittance T of a composite with a TiO₂ coating is displayed in Fig. 1.

The thickness and refractive index of the film were measured by means of spectral ellipsometry (Uvisel 2 scientific-spectrometric ellipsometer). The specular reflection coefficient R of the composite was calculated from the expression [10]

$$R = \frac{(n-1)^2}{(n+1)^2}, \quad (1)$$

where n is the measured refractive index of the film.

The light losses A in the coating were determined as the difference

$$A = 100 - T - R. \quad (2)$$

The scattering losses associated with the roughness of the surface and the imperfections of the film enter into the value of A . In our opinion the coating obtained by deposition from colloidal solutions comprises a frame consisting of particles of the pore-permeated solid phase of the sol. The pores are formed as a result of more or less close packing of the particles in the layer. The packing density, size and volume fraction of the pores are determined by the dispersity of the sol particles and the flow regime of the film-forming solution relative to the substrate, which depends on the deposition rate.

DISCUSSION

It is well known that the refractive index n_{eff} of a solid porous body is related with the porosity Po by the relation [11]

$$n_{eff} = n_1 - Po (n_1 - n_3) - (n_2 - n_3) f(P/P_o), \quad (3)$$

where n_1 , n_2 and n_3 are the refractive indices of the material comprising the frame of the layer, the adsorbed water and the air, respectively; Po is the porosity; and, $f(P/P_o)$ is the equation of the adsorption isotherm in general form.

If it is assumed that for the same packing density of the particles of the solid phase in a nanolayer the number of pores will grow as the thickness of the layer, it can be expected that there exists a relation between the refractive index and thickness of the film. Figure 2 confirms this supposition and shows that the refractive index decreases with increasing coating thickness. In addition, a very reliable inverse relation, described by a linear equation with curve fitting accuracy close to 0.8, is observed for silicon dioxide films. It should be noted that for TiO₂ the relation is unreliable; the tendency of the refractive index to decrease with increasing film thickness can be explained by greater nonuniformity of the coatings compared with SiO₂.

Analysis shows that the difference of the properties of composites and films deposited on the opposite sides of float-glass is predetermined by the difference in the chemical composition and, therefore, the properties of the substrate sides which during ribbon production come into contact with

the tin melt (tin side) or the protective gas atmosphere (gas side) of the melt tank.

Experiments show that the thickness of the coatings obtained by deposition from solutions depends largely on process parameters such as the content (by weight) of the oxides in sols and their rate of deposition on the substrate (Table 2).

SiO₂-Coated Composites. As the silicon dioxide content in the solution increases, the kinematic viscosity of the solution, proportional to the volume fraction of the disperse phase, increases consistently. The light transmittance of the film-forming solution and composite decreases with increasing number of light-scattering solid particles of the sol, which is one reason for the degradation of the continuity of the coating. The film thickness increases and the refractive index decreases for the reasons examined above.

TiO₂-Coated Composites. If the particles of the disperse phase SiO₂ of the sol are nearly pseudo-spherical, then, as studies show [8], TiO₂ tends to form nanotube-chains. Sols containing TiO₂ easily form precipitates and are sensitive to the content of the hydrolysis catalyst (acid) and water, brought in together with the solvent and concentrated hydrochloric acid. In choosing film-forming solutions with different concentrations the authors followed the recommendations in [12]. As a result the actual relation between the volume amounts of tetraethoxytitanium and hydrochloric acid in sols is not the same: 29 and 19 for FFS with 2.5 and 5% oxide, respectively. Therefore, the maturation dynamics of the solutions is different: on the 10th day of storage the sol with 2.5% oxide thickened and transformed into gel, while the sol with 5% oxide remained stable and retained transmittance for 6 months.

Evidently, the reduction of viscosity and light transmittance of the solution with increasing TiO₂ content is explained by the particulars of the maturation process and the shape of the particles in the disperse phase.

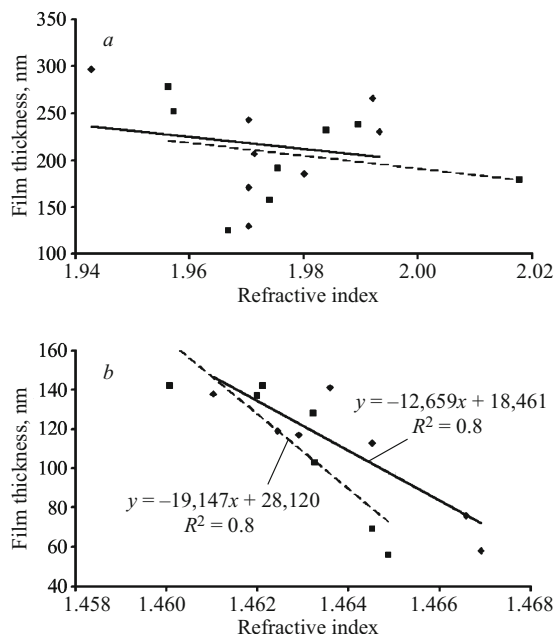


Fig. 2. Relation between the refractive index and thickness of SiO₂ (a) and TiO₂ (b) films. The measurements were performed on the 'tin' (solid line) and 'gas' (dashed line) sides of the composite substrate.

The small increase obtained in the refractive index of the coating as a result of the deposition of FFS containing 5% TiO₂ is probably due to diffusion of sodium, calcium and silicon oxides from the substrate into the film and changes in the film composition and refractive index. A procedure proposed by L. I. Demkina for glass [9] was used to calculate the increases Δn in the refractive index of the composite due to the penetration of the components from the substrate into the film. For composites with coatings obtained by depositing FFS containing 2.5 and 5% TiO₂, the expected incre-

TABLE 2. Properties of Films and Composites as Functions of the Oxide Content in the Film-Forming Solution

Oxide content, wt. %	Film-forming solution (FFS)		Film*		Composite*	
	Viscosity, mm ² /sec	Light transmittance, %**	<i>n</i>	<i>h</i> , nm	<i>T</i> , %	<i>A</i> , %
Coating with SiO ₂ ***						
2.5	1.82	88.0	1.4666	76	91.2	8.8
5.0	2.10	87.1	1.4636	141	90.4	9.6
7.5	2.91	85.7	1.4579	331	89.6	10.4
Coating with TiO ₂ ***						
2.5	4.75	74.0	1.9703	130	76.7	12.7
5.0	2.97	2.0	1.9713	207	69.7	19.6

* The measurements were performed on the 'tin' side of the float-glass substrate.

** At wavelength 400 nm.

*** The maturation time of the FFS and the deposition rates are, respectively, 47 days, 5.8 mm/sec for SiO₂ and 3 days, 3.8 mm/sec for TiO₂.

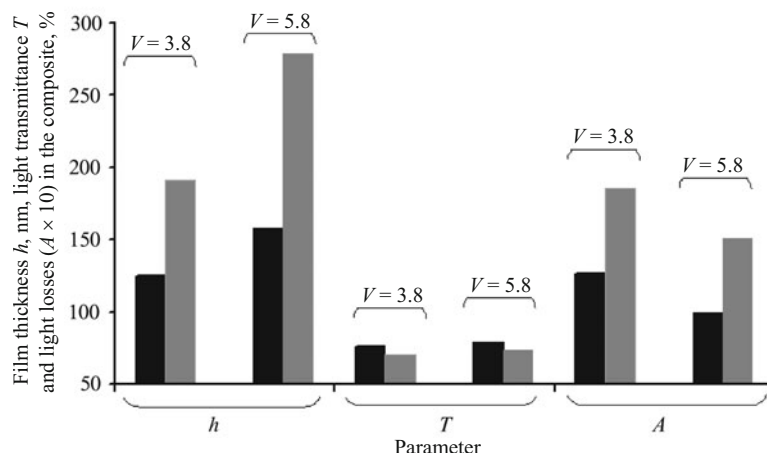


Fig. 3. Histogram of the change in the properties of coatings and composites obtained by deposition of solutions containing 2.5% SiO₂ (black columns) and 5% SiO₂ (gray columns) for different deposition rates: 3.8 and 5.8 mm/sec (the numbers are indicated above each column pair). The measurements and determinations were made on the 'gas' side of the substrate.

ments Δn relative to the substrate were 0.344 and 0.847, respectively; this is in line with the change in the measured values of n .

The dependence of the coating thickness and the light transmittance and losses of the composite on the TiO₂ content in the solution deposited is identical to that for a solution containing SiO₂.

The effect of the deposition rate on the characteristics of the coatings and composites is shown in Table 3.

The coating thickness is proportional to the deposition rate, the value of n remains practically unchanged to within the limits of the experimental error, and a tendency for n to decrease is observed only at the maximum deposition rate

TABLE 3. Dependence of Some Characteristics of Films and Composites on the Deposition Rate of Film-Forming Solutions Containing 2.5% Oxides

FFS deposition rate, mm/sec	Film*		Composite*	
	n	h , nm	T , %	A , %
Coating with SiO ₂ **				
3.8	1.4649	56	91.3	3.56
5.8	1.4645	69	91.8	3.55
17.3	1.4621	142	88.7	3.52
Coating with TiO ₂ ***				
3.8	1.9667	125	76.7	12.7
5.8	1.9740	158	79.2	10.4
17.3	1.9572	252	72.5	17.0

* The measurements were performed on the 'gas' side of the substrate.

** The maturation time of the solution is 47 yr.

*** The maturation time of the solution is 3 days.

17.3 mm/sec. It is possible that this can be explained by the change in the flow regime of the solution relative to the substrate and some increase in the level of turbulence of the solution, which keeps the disperse particles from being packed into a uniform layer. The light transmittance reduction, which is sharper for composites containing TiO₂, serves confirm this supposition.

Figure 3 demonstrates the overall effect of the solution deposition rate and the oxide content of the solution on the properties of coatings and composites.

When the two named parameters increase simultaneously (compare the first black and last gray column of the histogram for a particular parameter) the coating thickness increases significantly (see Fig. 3) and the refractive index n decreases from 1.9667 to 1.9562, respectively, for films obtained by depositing FFS containing 2.5% oxides at the rate 3.8 mm/sec and FFS containing 5% oxides at the rate 5.8 mm/sec. The light transmittance of the composites decreases while the light losses increase consistently (see

Fig. 3). In our view this phenomenon can be explained by an increase in the porosity of the film, which depends on the size and number of particles in the disperse phase of the sol as well as on the regime of the particle motion relative to the substrate, which is related with the deposition rate.

The next parameter significantly affecting the properties of coatings and composites is the solution maturation time. In this case hydrolysis, polycondensation and agglomeration processes develop in the sols, as a result of which the amount and form of the disperse phase can change and even precipitates can form.

The properties of solutions and composites are listed in Table 4.

An increase in the maturation time results in a small decrease of the solution viscosity, so that the volume fraction of

TABLE 4. Effect of the Maturation Time of the Solutions (FFS) on the Main Properties of Coatings and Composites

Film-forming solution			Film*		Composite*	
Maturation time, days	Viscosity, mm ² /sec	Light transmittance, ** %	n	h , nm	T , %	A , %
FFS containing 5% SiO ₂						
47	2.10	87.1	1.4633	103	89.2	3.54
67	2.00	83.8	1.4632	128	91.0	3.54
81	2.02	87.1	1.4601	142	92.9	3.50
FFS containing 5% TiO ₂						
3	2.97	2	1.9754	191	70.7	10.8
14	2.96	74	2.0036	209	76.4	11.2

* The deposition rate of the solution on the substrate is 3.8 mm/sec; the measurements were performed on the 'gas' side of the substrate.

** At wavelength 400 nm.

the disperse phase remains practically unchanged. However, the particle shape and size change. For example, the nanotubes in the titanium dioxide coating decrease somewhat in length and cross section, which correlates with an increase in the light transmittance of the solution and composite (see Table 4). An increase in the maturation time also brought an increase in the film thickness.

Since the refractive index of a coating is the result of a superposition of factors such as the porosity of the layer and the mass fraction of the oxides migrating from the substrate, the effect of the maturation time of the solution on this parameter is ambiguous.

CONCLUSIONS

1. The difference in the properties of composites and films deposited on the opposite sides of float-glass is predetermined by the difference in the chemical composition and properties of the sides of the substrate.

2. The refractive index of the SiO_2 coatings decreases with increasing thickness of the layer.

3. An increase in the mass fraction of film-forming oxides, deposition rate and maturation time of solutions (FFS) always results in an increase of the thickness of the coating and degradation of the light transmission of the composites. The effect of these parameters on the refractive index of the films is not always unique, because n largely depends on the porosity of the coating, which is determined by the technological parameters examined in the article as well as by the modification of the film composition by the components penetrating from the substrate.

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